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Effect of temperature on the spectral properties of InP/ZnS nanocrystals

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Abstract. Optical absorption (OA) and photoluminescence (PL) spectra of InP/ZnS core/shell nanocrystals with 2.3 nm average size were investigated in the temperature range of 6.5–296 K. Using second derivative spectrophotometry technique energies of the OA transitions at 296 K in quantum dot (QD) solutions and films are evaluated to be E_1 = 2.37, E_2 = 4.10 and E_3 = 4.68 eV. Temperature shifts of the E_1 and E_2 levels are found to result from interaction with effective phonons of 59 and 37 meV energies, respectively. Herewith the 370 meV half-width of the first exciton absorption peak remains constant due to the dominance of inhomogeneous broadening effects caused by QD parameters distribution. Measured PL spectra have a complex structure and can be described in 6.5–296 K range by two independent Gaussian components associated with exciton and defect-related states. In addition, Stokes shift of 320 meV is observed to decrease at T > 200 K. PL thermal quenching analysis in frame of Mott mechanism points to presence of non-radiative relaxation channel with an activation energy of 74 meV.

1. Introduction

Great interest has been focused on $A^{III}B^{V}$ colloidal quantum dots (QDs) since they possess tunable size-dependent optical properties and low toxicity. Among this group, InP QDs coated with zinc sulfide shell exhibit characteristics good enough to substitute environmentally restricted Cd-based counterparts [1,2]. It makes InP/ZnS QDs promising both in optoelectronic and biocompatible applications on an industrial scale [3,4]. At the same time, optical properties of InP/ZnS nanocrystals remains insufficiently studied both from the standpoint of experimental analysis and consistent theoretical justifications. In this regard, temperature-dependent optical absorption (OA) and photoluminescence (PL) measurements could help to obtain valuable information on emission and absorption exciton states. To date, there are several studies reporting the temperature analysis of InP/ZnS PL spectra and investigating their band-edge exciton fine structure [5–7]. Previously, we have studied OA temperature dependence in QDs of 2.1 nm average diameter [8,9]. This work aims to investigate temperature behavior of OA and PL spectra of larger InP/ZnS QDs of 2.3 nm size in the range of 6.5–296 K.

2. Samples and Techniques

InP/ZnS colloidal QDs under study marked as DS-72b were synthesized by Institute of Applied Acoustics (Dubna, Russia). They have three-layered structure: the core made of InP, the shell made of ZnS, and the coating of modified polyacrylic acid. Semiconductor nanocrystals were dispersed in water with initial concentration of 48.4 g/l. An average core diameter estimated from the first exciton

energy [10] is 2.3 nm. Quantum yield of the nanocrystals was determined using relative procedure with Rhodamine 6G as a reference [11] and amounted to 10 %.

Optical absorption measurements of samples were carried out in a range from 190 to 900 nm by means of a Shimadzu UV-2450 spectrophotometer. Solutions of different concentrations were investigated at room temperature (RT) in a quartz cuvette with 1 cm optical path. To establish the temperature dependence of the nanocrystals OA spectra, we used InP/ZnS film formed by physical deposition of the initial colloidal solution at room temperature on a quartz substrate with a thickness of 1 mm. The substrate transmission is 94 % in the 300-900 nm range smoothly decreasing to 85 % at 190 nm. Absorption spectra at T = 6.5–296 K were measured using a combined installation based on the Shimadzu UV-2450 spectrophotometer and a Janis closed cycle refrigerator system, model CCS-100/204N, equipped with a DT-670B-CU temperature sensor and Model 335 controller. A HiCube 80 Eco turbo pumping station maintained vacuum inside the cryostat ($7 \cdot 10^{-5}$ mbar). The spectra were registered at the following temperature values: 6.5 K, over the range from 10 to 100 K in 10 K, and in the range of 100–296 K with a temperature step of 20 K. A slit width and sampling interval were set to the 2 and 0.5 nm, respectively.

Photoluminescence spectra of the QDs were analyzed for InP/ZnS film in the range 6.5–296 K. For this purpose, the described refrigerator system was coupled with Andor Technology Shamrock SR-303i-B spectrograph and Newton^{EM} DU-970P-BV-602 CCD-camera. LED with emission maximum at 372 nm was used as an excitation source.

3. Results

Figure 1 shows optical absorption spectra for solutions of InP/ZnS QDs with 40 and 1.25 g/l concentrations as well as for films at 6.5 and 296 K. For clarity, the data is presented in semilogarithmic coordinates. Three features, indicated by arrows in figure 1, can be distinguished on spectra. E_1 and E_2 shoulders in the ranges of 490–570 nm and 290–330 nm, respectively, are observed for all samples in the solution and film form. The E_3 feature in the range of 250–280 nm appears only for solutions with a low concentration. As for the temperature behavior of the spectra, the positions of the optical transitions are shifted toward higher energies when T is lowered. Simultaneously, the optical density increases within the investigated wavelength range.

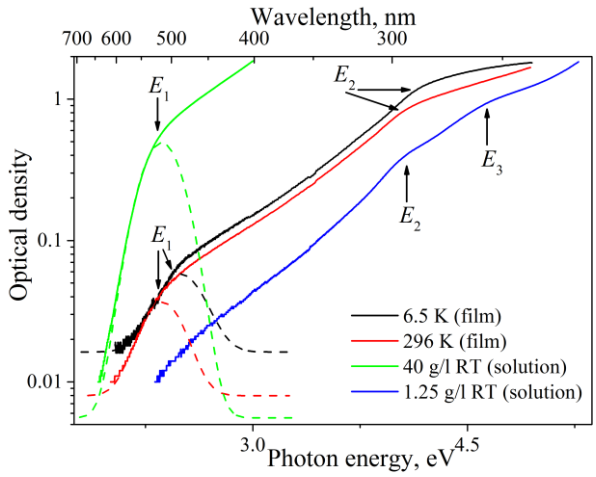

Figure 1. OA spectra of the InP/ZnS at various concentrations and temperatures. Dashed lines represent Gaussian approximation of the first exciton band.

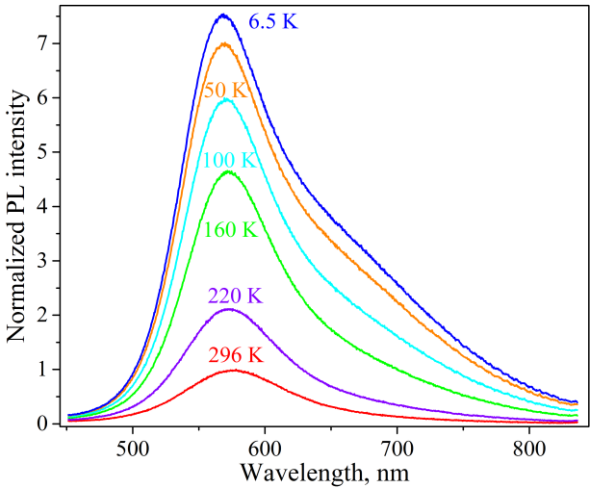

Figure 2. PL spectra of the InP/ZnS at various temperatures.

Figure 2 shows the photoluminescence spectra of the InP/ZnS film registered at different temperatures. The PL intensity is normalized to the maximum value at room temperature. It is seen

that the luminescence spectrum at RT is an asymmetric band with a maximum at a wavelength of λ_{max} = 578 nm. Upon temperature decreasing, the peak moves to shorter wavelengths and λ_{max} = 569 nm at 6.5 K. The intensity at the maximum increases by 8 times when temperature drops from 296 to 6.5 K. Note that below 100 K one can clearly observe a spectral shoulder in the range of 630–740 nm.

4. Discussion

4.1. Optical absorption and exciton-phonon interaction

The OA features, indicated by arrows in figure 1, reflect the transitions between the quantized exciton energy levels of nanocrystals. They manifest themselves on a monotonically increasing background associated with the contribution of high-energy states, scattering and other processes. Determination of such hidden bands was carried out using the second derivative of the absorption spectra [9]. Figure 3 illustrates this procedure for the calculation of E_1 and E_2 energies for the case of the InP/ZnS film absorption spectra at 80 and 220 K. Table 1 shows the obtained values. It should be noted that the optical transition energies in solutions do not depend on concentration and coincide with the estimates for the film at room temperature within ±0.02 eV experimental error. The absence of the E_3 = 4.68 eV transition in the film spectra may be associated with the cooperative phenomena in QD arrays, since change in the distance between them during deposition leads to a modification of their energy structure [12].

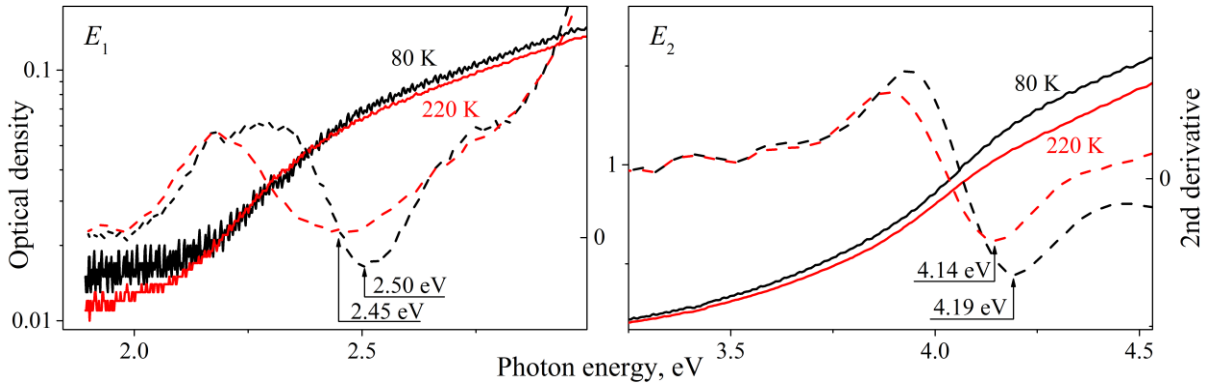

Figure 3. OA spectra (solid lines) and their second derivatives (dash lines) for InP/ZnS film.

As in our work [9], for the quantitative analysis of the experimental dependences E_1 (T) and E_2 (T), we used Fan expression for the temperature behavior of the energy gap E_g in crystals [13]:

$$E_g(T) = E_g(0) - A_F\left[\exp\left(\frac{\hbar\omega}{kT}\right) - 1\right]^{-1}, \quad (1)$$

as well as a semi-empirical linear model:

$$E_g(T) = E_g(0) - \beta T. \quad (2)$$

Here $E_g(0)$ is the energy of the optical transition at 0 K, eV; A_F is the Fan parameter that depends on microscopic properties of material [13,14], eV; $\hbar\omega$ is the effective phonon energy; k is the Boltzmann constant, eV/K; β is the energy gap temperature coefficient, eV/K. As previously demonstrated in [13], in the limit of high temperatures ($kT \gg \hbar\omega$), the relation (1) reduces to (2), with the temperature coefficient being written as:

$$\beta_\infty = A_F \frac{k}{\hbar\omega}. \quad (3)$$

Figure 4 shows approximations of the experimental $E_1(T)$ and $E_2(T)$ dependencies using the Fan relation (1) (blue solid lines) and the linear model (2) (blue dash lines). The obtained parameters are given in table 1. The displacement of the E_1 and E_2 energy levels is found to be due to the interaction with different effective phonon modes. The Huang-Rhys factor S proportional to the strength of the electron-phonon coupling [5,6] and related to A_F as $S = A_F/2\hbar\omega$ [9], is 2.4 times larger for the E_1 band. Figure 4 also represents the dE_g/dT data (red dash lines), which characterizes the change in the temperature coefficient β. The dash-dot lines correspond to the β_∞ level calculated according to expression (3).

For the first exciton absorption peak we also estimated the full width at half maximum H. For this purpose, the low energy region of spectra was approximated by a Gaussian band centered at E_1, see the dashed lines in figure 1. The calculated values showed that the H does not change in the investigated temperature range and amounts to 370±30 meV. Such a result indicates the dominance of the inhomogeneous broadening caused by the distribution of studied nanocrystals in the ensemble in size, shape, imperfections, etc. [9,10,15].

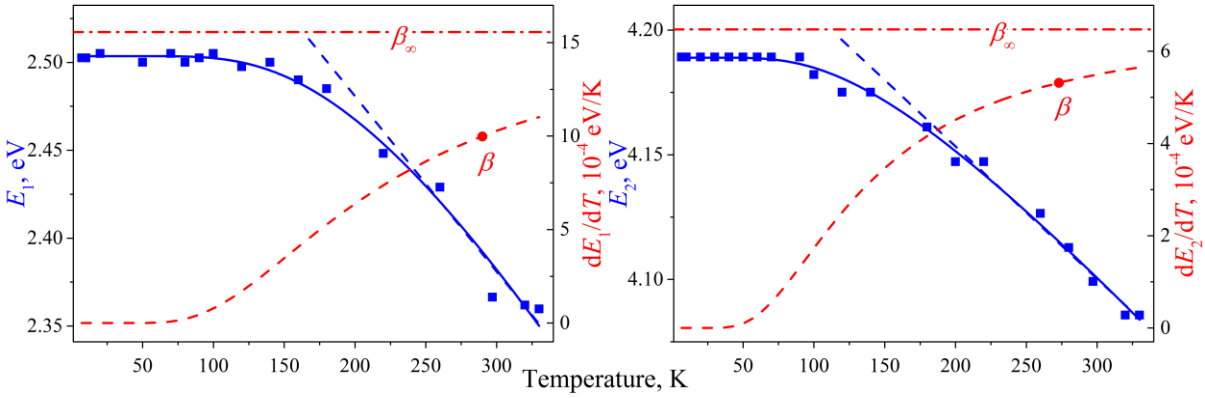

Figure 4. Temperature dependencies for E_1 and E_2. Blue square symbols are our experimental estimates.

Table 1. OA parameters of InP/ZnS QDs.

Optical transition	E, eV at 296 K	H, meV at 296 K	E, eV at 6.5 K	H, meV at 6.5 K	A_F, eV	$\hbar\omega$, meV	S	β, 10^{-4} eV/K	β_∞, 10^{-4} eV/K
E_1	2.37	365	2.49	359	1.06	59	9.03	9.97	15.56
E_2	4.10	–	4.19	–	0.27	37	3.76	5.31	6.47

4.2. Exciton and defect-related photoluminescence

All measured PL spectra of InP/ZnS in the investigated temperature range were deconvoluted with a high accuracy (Adj. R-square > 0.999) by two components of a Gaussian shape. Figure 5 shows the approximation examples of experimental data at 6.5 and 296 K. In [16] luminescence spectra of InP/ZnS nanocrystals with a 2 eV emission maximum at 300 K were successfully approximated by two components of a Lorentz shape. The E_{exc} component can be associated with exciton states and the E_d band related to defect states of the QD crystal structure. The exciton energy demonstrates typical blueshift under cooling as presented in figure 6. However, it cannot be fitted with expression (1) owing to the feature in a range of 200–240 K. The defect-related peak is redshifted having temperature-independent half-width of H = 600±20 meV. These facts indicates a possible more complex structure of the PL band and the need to identify origin of the components for an adequate description of the observed temperature behavior.

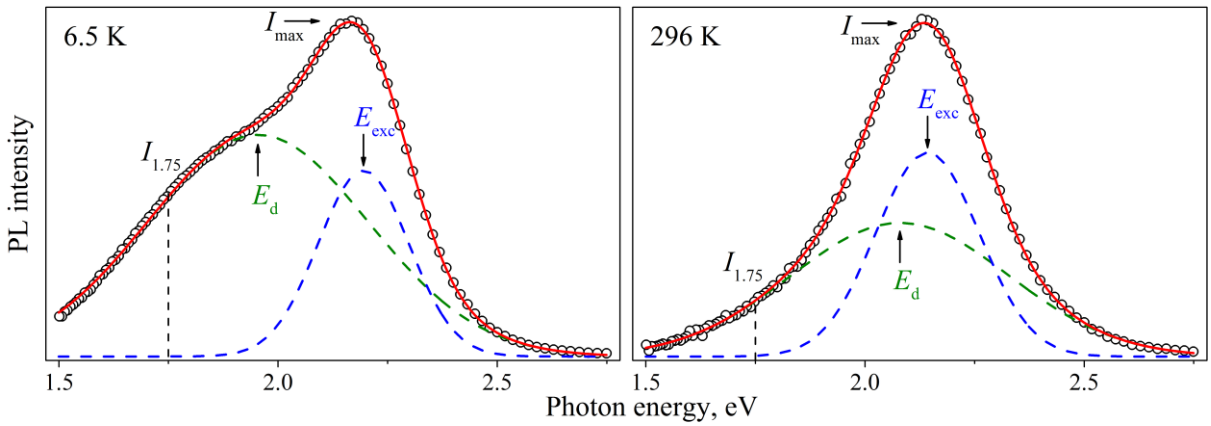

Figure 5. Deconvolution of PL spectra at 6.5 and 296 K. Symbols represent experimental data, solid red lines are fitted curves, dash lines are exciton E_{exc} and defect-related E_d components.

Figure 6 inset shows the temperature dependence of the Stokes shift calculated as $E_1 - E_{exc}$. It is noticed to be almost independent of temperature in the 6.5–200 K range, and then its value begins to decrease. This behavior may be due to the fine structure of exciton emission. The quantum confinement effect enhances the spin-exchange interaction and leads to an increase in the splitting between bright and dark exciton states. The contribution of the dark state with a lower energy to the PL band is maximal at low temperatures. Population of the bright exciton level grows with temperature eventually resulting in a decrease of the Stokes shift from 320 to 220 meV at $T > 200$ K [17].

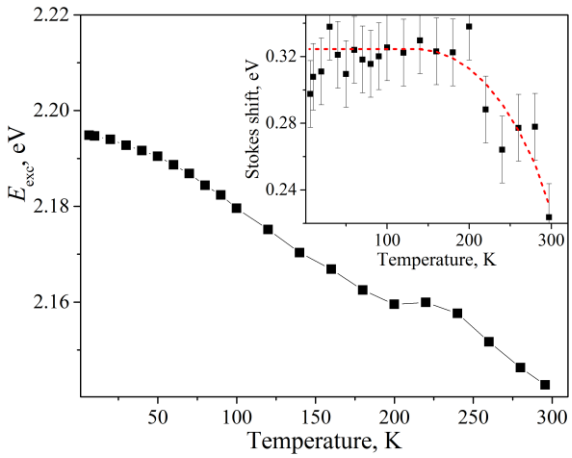

Figure 6. Temperature dependence of the E_{exc} and Stokes shift (inset). Dash curve is guide for the eye.

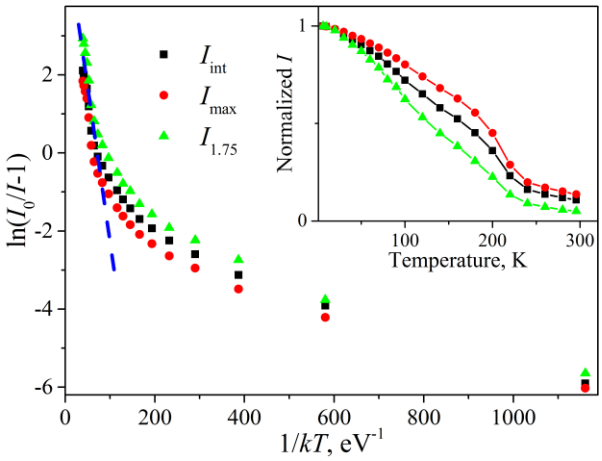

Figure 7. PL temperature quenching. Dash line shows linear approximation.

4.3. PL thermal quenching

To analyze the processes of PL thermal quenching, three parameters were taken: an integrated intensity (I_{int}), luminescence intensities at spectrum maximum (I_{max}) and at 1.75 eV ($I_{1.75}$) which corresponded to the E_{exc} and E_d components (see figure 5). Figure 7 inset shows the PL quenching curves for these quantities normalized at 6.5 K. They exhibit different character of intensity drops with T. Nevertheless, in Arrhenius coordinates it can be seen that all dependencies have a common linear region (dash line), which slope determines the activation energy E_a of PL quenching in frame of Mott relation [18,19]. Thus, there is a common non-radiative relaxation channel above 150 K with E_a =

74±6 meV. Quenching in the low-temperature region cannot be described with a linear function, which points a more complex mechanism.

5. Conclusion

The temperature dependencies of the optical absorption and photoluminescence spectra of the InP/ZnS core/shell QDs with an average diameter of 2.3 nm were studied in a range of 6.5–296 K. Three optical transitions with energies of E_1 = 2.37, E_2 = 4.10 eV and E_3 = 4.68 eV are shown to appear in the spectra of QD solutions and films at room temperature (RT). Analysis of the E_1 and E_2 temperature shifts in the framework of the Fan formalism showed that they are caused by interaction with effective phonons of 59 and 37 meV energies, respectively. Herewith, the half-width of the first exciton absorption peak equals to 370±30 meV and does not change due to the dominance of inhomogeneous broadening resulting from QD distributions in size, shape, imperfections, etc.

Photoluminescence is characterized by broad emission band with 2.14 eV maximum at 296 K. All spectra measured in the 6.5–296 K range are deconvoluted into two components of a Gaussian shape with 2.14 and 2.08 eV maxima at RT. They are assumed to originate from exciton and defect-related states, correspondingly. A PL quenching analysis in frame of Mott relation indicates that there is a common non-radiative relaxation channel with an activation energy of 74 meV. In addition, a decrease in the Stokes shift is observed from 320 to 220 meV at T > 200 K implying large energy splitting between dark and bright exciton states.

Acknowledgments

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